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Wetting Agents in Textile Processing

I. STRUCTURE AND SURFACE ACTIVITY

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THE term "wetting agent," as used here, signifies a compound which is soluble or semi-soluble in water and which, when dispersed in water, facilitates the wetting-out of materials and the spreading of water upon surfaces.

In order to wet the surface of a solid, water must displace air from that surface. That is, a solid-air surface or interface must disappear and an equal area of a solid-liquid interface must be formed. This will occur spontaneously when the solid is brought into contact with water *provided* the free surface energy* of the resulting interface is less than that of the interface which disappears. For *immersional* wetting, this difference, the decrease in the free surface energy of the system, may be considered a measure of the tendency of the liquid to wet the surface and, in general of the rate at which wetting will occur. In the case of *spreading* wetting an additional factor is involved, namely, the increase in the surface of the liquid in contact with air. That is, spreading is also opposed by the surface tension of the liquid itself. These relations are more clearly expressed by the simple equations:

(1) For immersional wetting, $F = S_1 - S_{12}$

(2) For spreading wetting, $F = S_1 - (S_{12} + S_2)$.

In these equations F represents the decrease in the free surface energy of the system; S_1, S_{12}, and S_2 represent the free surface energies of the solid-air, solid-liquid, and liquid-air interfaces respectively. A thorough discussion of the factors involved in different types of wetting and their evaluation has been published by Osterhof and Bartell[1].

Probably no field of textile chemistry has recently attracted more attention than that of wetting-out agents, penetrants and dyeing assistants. Activity in the investigation of this type of compounds has been greatly stimulated through the relatively large number of new compounds answering to this description which has been introduced during the last few years.

In a series of three articles of which this is the first, Professor Harvey A. Neville of Lehigh University and his associates record some recent research work which we believe not only has an important bearing upon the mechanism of wetting-out and softening reagents, but will also serve an educational purpose.

A dissolved substance which lowers the surface tension of a liquid (toward air) will, in general, tend to lower its interfacial tension toward a solid. It is obvious from equations (1) and (2) that lowering the surface tension of the liquid and the solid-liquid interfacial tension favors spreading and wetting. Substances which confer these properties upon water are therefore useful in all types of wet processing of textile materials. Their effects result from the concentration and orientation of the substances at surfaces and interfaces. They may be thought of as providing a bond of attraction between the fiber and the liquid with which it is being treated.

During the past few years there have been developed and marketed a great number of such compounds for use in the textile and leather industries. These products have been recommended as wetting-out agents, penetrants, emulsifying and scouring agents, dye assistants and levelers, carbonizing aids, and for various other special applications. In general, these substances are organic compounds containing an active polar, hydrophilic or "water-soluble" group. Usually they are sodium salts of either sulfonic acids or acid sulfuric esters. The so-called "sulfonated" higher alcohols, recently discussed by Killefer[2], are of the latter type. The organic chain or hydrophobic group in these wetting agents must be sufficiently large to prevent a high or complete solubility of the molecule in

*Free surface energy is expressed in ergs per squar centimeter and is numerically equal to the surface (or interfa al) tension measured in dynes per centimeter.

water. These compounds are, therefore, similar to the alkali soaps in structure and, like the soaps, they form colloidal solutions in water. Like soap, they are very active surface-tension depressants, they stabilize foams, and have detergent and emulsifying ability. They offer certain advantages over soap in that:

1. Due to absence of hydrolysis, their water solutions have a much lower alkalinity than soap—usually giving a pH of 7 as compared with about pH 10.6 for soap.

2. They may be used in acid solutions as their free acids are soluble.

3. They are not affected by hard water as their calcium and magnesium salts are soluble.

Thus the newer type of wetting agent may be considered for use in place of soap in ordinary operations, or it may find applications in processes in which the use of soap would be prohibited—for example, if it is found to be advantageous to operate a process at a pH less than 10. In the first case, the high cost of these materials compared to that of soap must be considered, taking into account the required concentrations and relative efficiencies of the two types of products. In the second case, the potential user should determine the specific action of the wetting agent under the conditions of the operation, the minimum effective concentration required, and the rate at which it is exhausted from the bath. These factors will receive some attention in this discussion.

As indicated above, the ability of a substance to lower the surface tension of water is fundamentally related to its action as a wetting agent. It is therefore of interest to study this important property of those types of compounds which find application as wetting agents.

The surface activities of members of the homologous series of aliphatic acids and their sodium salts have been reported by various investigators[3]. These substances show, in general, increasing surface activity, or ability to lower the surface tension of water, with increase in length of the carbon chain, in agreement with Traube's rule. In these substances the polar (water-soluble) group is the carboxylate group and the soaps belong to this class. The measurement of the surface activities of some sulfonates of the benzene series was undertaken by the authors of this paper to show the influence of the nature of the substituent alkyl group and of its position in the benzene nucleus in relation to the polar sulfonate group.

Preparation of Aromatic Sulfonates

True sulfonic acids of the aromatic hydrocarbons and the sodium salts of these acids may be readily prepared in a pure condition. They may be considered typical of the sulfonated wetting agents although the lower members of the series will not lower the surface tension of water sufficiently to have practical application in this field.

The sulfonation of benzene, toluene, xylene and cymene was accomplished by the general method of Gatterman[4] using fuming sulfuric acid and the minimum temperature required for each reaction. The sodium sulfonate was precipitated by treating the reaction products with saturated sodium chloride solution, or was obtained by neutralization with sodium hydroxide and evaporation. The sodium sulfonate was then purified by recrystallization from absolute alcohol or acetone until it was free of sulfate. Acetone was the more effective medium for the purification of the higher members of the series. Ethyl benzene, isopropyl benzene and butyl benzene were prepared by the Fittig synthesis[5], were then sulfonated, and their sodium salts obtained and purified as described above.

Surface Tension Measurements

Solutions of these salts in distilled water were prepared and their surface tensions were measured over a range of concentrations at a constant temperature of 18° C. These measurements were made by means of an improved torsion balance which was fully described by De Gray in a recent article[6]. The static or equilibrium surface tension values for these solutions are shown in Fig. 1.

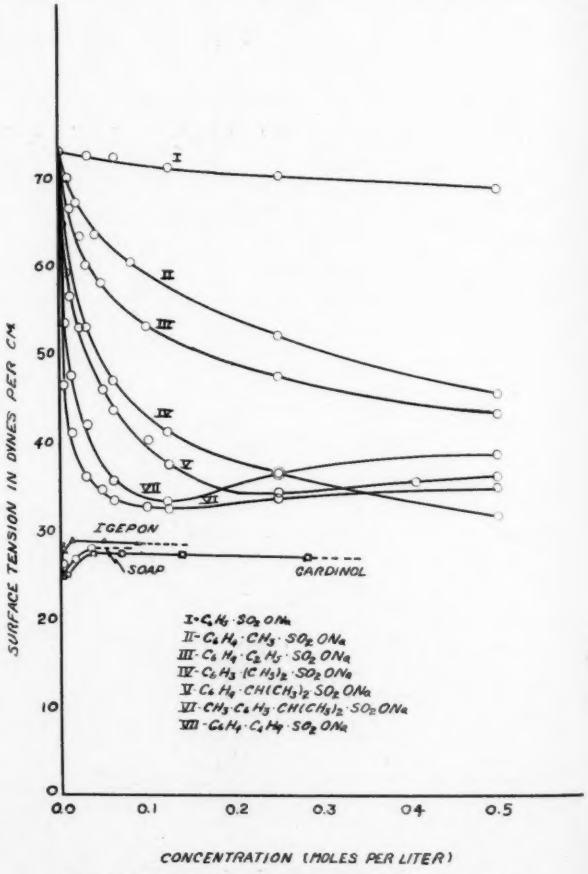

Fig. 1—Surface Activity of Sulfonates and Wetting Agents.

In the case of the first member of the series, sodium benzene sulfonate, the observed lowering of the surface tension of water is roughly proportional to the concentration of the solute. In this its effect is similar to that of the lower members of the aliphatic acids or their salts and, in general, of substances in true solution which decrease surface tension. Beyond this first member the curves show an increasing tendency to sag or to deviate from the

straight-line relationship as the alkyl substituents increase in length or complexity. It is of interest to note that although the sulfonates of ethyl benzene (curve III) and xylene (curve IV) are identical in molecular weight, the latter is considerably more effective in lowering the surface tension of water. This indicates that two substituent groups increase the surface activity of the compound more than a single group containing the same total number of carbon atoms. This principle is exemplified further in the curves for the sulfonates of butyl benzene (curve VII) and cymene, or para methyl isopropyl benzene, (curve VI). These two curves also exhibit a minimum which is a characteristic property of active surface-tension depressants and usually indicates a colloidal condition of the solute.

Maximum Surface Activity

The surface tension-concentration curves for the commercial wetting agents, soap, Gardinol and Igepon, are also shown in Fig. 1. These very active surface tension depressants show characteristic inima and effect what is probably the greatest possible lowering of the surface tension of water for dilute solutions. Their minimum surface tension values probably correspond to a water surface saturated or completely covered by the organic ions of the wetting agent. These ions are oriented perpendicularly to the surface of the water, the polar group being in the water and the hydrocarbon chain extending into the air. Thus the exposed surface in each case consists of the methyl groups at the non-polar end of the molecules; and the minimum surface tension value should be approximately the same for all aliphatic components of this type provided the hydrocarbon chain is of sufficient length.

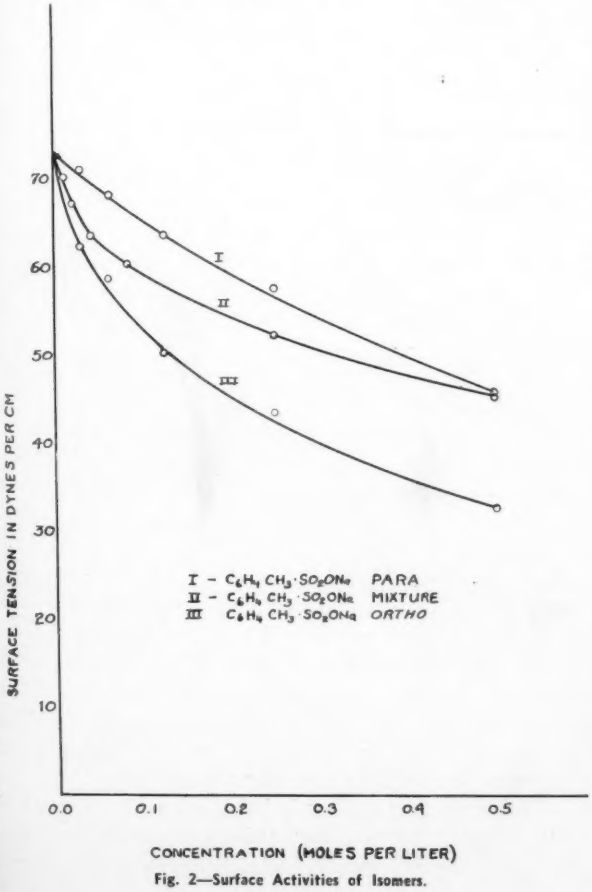

Fig. 2—Surface Activities of Isomers.

Surface Activity of Isomers

It has already been pointed out that isomers having two substituent groups have a greater surface activity than those containing a single group with the same total number of carbon atoms. A different type of isomerism must also be considered due to the possibility of forming the several isomeric sulfonates in some cases by the combination of sulfuric acid at the ortho, meta or para position. With the exception of sodium benzene sulfonate, the solutes represented by the numbered curves in Fig. 1 are probably mixtures of isomers.

In the sulfonation of toluene a mixture of two isomers is obtained. This mixture is composed of approximately 70 per cent of the para and 30 per cent of the ortho isomer. These two isomers were separated by taking advantage of the different melting points of the corresponding toluene sulfonyl chlorides, according to the method recommended by Beilstein[7]. The ortho toluene sulfonate and para toluene sulfonate obtained from the separated sulfonyl chlorides were recrystallized from absolute alcohol and surface tension measurements were made upon the solutions of each. These results are shown in Fig. 2 in relation to the curve for the mixture of the two isomers. It will be observed that the ortho derivative is more effective than the para as a surface tension depressant and that in low concentrations the activity of the ortho isomer predominates in the mixture, while in more concentrated solutions the surface activity of the mixture approaches that of the less active para component.

References

[1]Osterhof, H. J. and Bartell, F. E., Jour Phys. Chem., *34*, 1399 (1930).
[2]Killefer, D. H., Ind. Eng. Chem., *25*, 138 (1933).
[3]Freundlich, "Colloid and Capillary Chemistry." E. P. Dutton & Co., New York, 1926. pp. 61-71.
[4]Gatterman, "Practical Methods of Organic Chemistry." Macmillan, 1915. p. 280.
[5]Ibid. p. 276.
[6]De Gray, R. J., Ind. Eng. Chem., Analyt. Ed., *5*, 70 (1933).
[7]Beilstein, "Handbuch der Organische Chemie," 4th Ed., Vol. XI, p. 83.

(To be continued)

NOTICE

A complete stenographic report of the A. A.T.C. & C. convention in Chicago last weekend will appear in future issue of the Reporter.

Kier Boiling, Peroxide and Sodium Hypochlorite Bleaching, and Anti-Chloring Cellulose Fabrics*

By MYRON W. ALLING

Kier Boiling

LOOSE cotton fibers thoroughly boiled out and bleached in the usual manner are harsh and unfitted for spinning, therefore, cotton piece goods are delivered to the bleachery in the grey state. They contain about 19.28% natural impurities and artificial sizing, of which 10.5% is starchy matter, 4.1% matter soluble in water, and 4.68% of substances most difficult to remove. This latter percentage which consists of motes, waxy matter, dirt, etc., is responsible for the high temperature (255.7° F.), the steam pressure (18.3 lbs.), the time (13 hours) and the caustic soda, soda ash, kier boiling assistant and silicate of soda required to have cellulose fabrics leave the kiers insured of the removal of all substances except cellulose.

*This is the second in a series of articles by the author, the first of which appeared on page 485 of the August 14th issue and was entitled "Sanding, Singeing, Wetting and Steeping Cellulose Fabrics."

Not alone does temperature, steam pressure, time and chemicals play the all-important part of size removal, but apparatus is just as important for the control of the requirements of kier boiling and for the confinement of the goods to be treated. We have, therefore, large vats or kiers equipped with various circulating systems which are designed to boil the goods under pressure and we have the open continuous kier which lends mechanical scouring power to the goods, which takes the place of steam pressure and the high temperature used in the boil. We will first consider the pressure kier with a constant and positive circulating system of the kier charge, as this is not such a recent development as the continuous kier.

The pump and heater type kier is desirable because it offers a constant and positive circulation of the liquor together with an accurate control of the strength and the temperature by the use of an outside heater and by thermostatic control which is not possible where direct steam is applied. See figure 1.

There are certain circulation systems which simply spray the liquor over the goods and it follows the course of least resistance through the great mass of cloth, which has a tendency to produce uneven results. There are other systems which divide the liquor as it leaves the outside heater into as many divisions as are required to give the best results. One part may be sprayed over the top of the center of the goods in the usual way, and the balance may be forced into any part of the goods in the kier from one or more perforated upright pipes, either in the center of the kier or in conjunction with several others placed at regular intervals along the side walls of the kier. This is known as the R. & H. circulation system and can be applied to any kier of the pump and heater type.

No matter what the conditions are, the greatest problem of kier boiling is to remove 4.68% of the substances which are so difficult of removal. Every textile machine company has its own pet kier, circulating system and whatnot to perform the work economically and effectively and today, with precision. Every bleacher does not know which of these is the best and neither does he know all of the functions which each chemical in his kier charge is supposed to perform, but he does know that there are specialists in these matters who do not use any rule-of-thumb methods in their recommendations, whether it be kiers or chemicals and he knows that they know the effectiveness of their own apparatus, and their own kier-boiling assistants, which can only be taken advantage of by constantly checking the old with the new.

Continuous kier boiling is based upon the removal of size through the cleansing action of alkaline solutions applied to the cloth mechanically, by spraying and squeez-

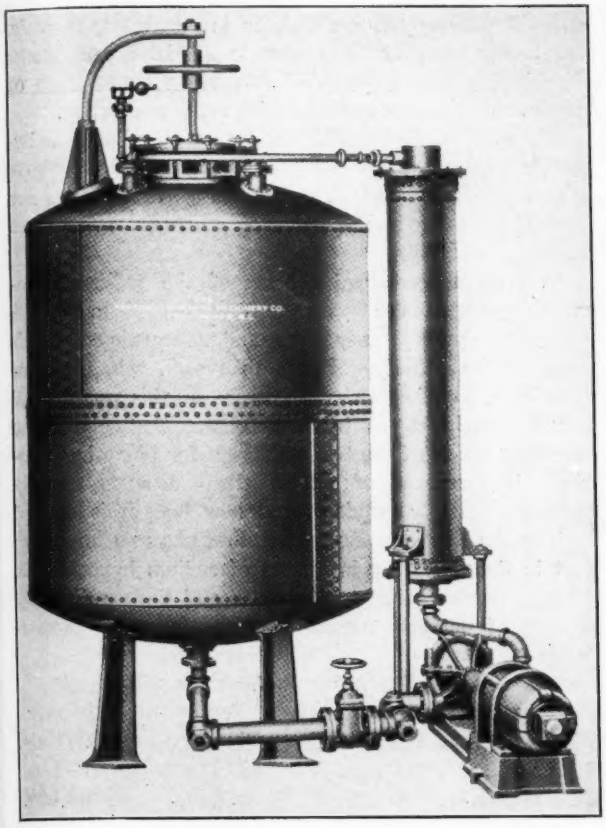

Figure 1

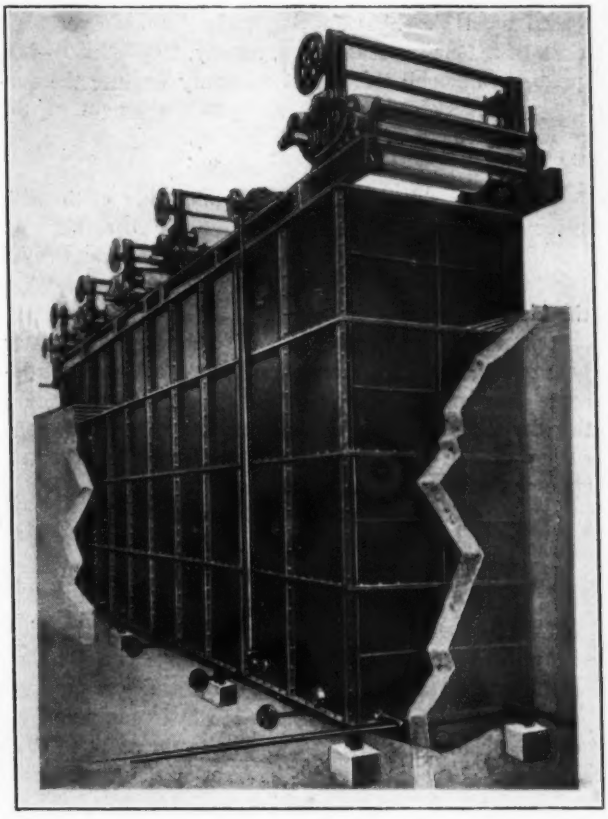

Figure 2

ing in a very deep ten-"J" box open washer with five sets of squeeze rolls. The machine is approximately 14 feet high, 5 feet across, and about 40 feet long. It is designed to run at any speed and it will handle all character of cotton fabrics in rope or open form—the rope running side by side through the machine, and, in the open form, one piece is superimposed upon the other. Many advantages are claimed for this type of machine and I believe, along with suitable penetrating, emulsifying, dispersing, and scouring agents that this is the forerunner for doing away with the old time, long drawn out method of kier boiling. See figures 2 and 3.

Most bleachers associate iron rust in their bleached cloth with kier boiling. The inside of the kier has always been a source of iron rust, especially if the sides have not been kept well coated. Mixtures containing white wash as a base have been more or less successfully used for this coating, but the method which I have found to be the most effective is as follows: If the kier is rusted badly, scrape, sandpaper, brush with a wire brush; then heat with steam, let dry, and paint with red oil. After eight hours paint again, then put 50 lbs. caustic soda and 40 lbs. red oil in the kier with 1,000 gallons water and boil with pressure over night. This method forms a good corrosion. If the kier is not badly rusted, add 100 lbs. silicate of soda and 40 lbs. red oil to the regular kier charge for about a week, at the end of this time the protective covering will be found sufficient to prevent further oxidation of the metal.

Bleaching Methods

In order to remove the discoloration of grey goods or goods that are in the raw state, even after they have been kier boiled or scoured on a boil-off machine, an active bleaching and oxidizing agent must be used in most cases to produce pure whites and beautiful shades. There are two important methods of bleaching, one is with peroxide and the other is with sodium hypochlorite. We will first consider the peroxide method, and in order to be specific both of the methods given below will be

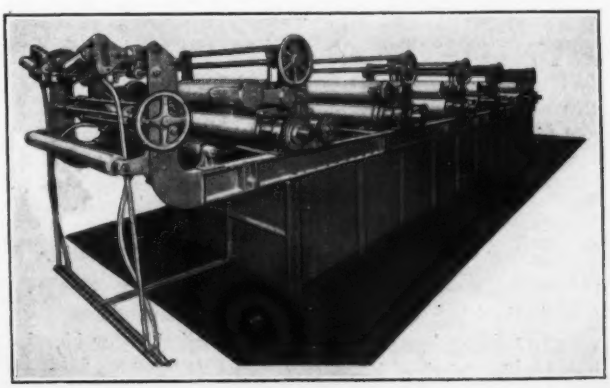

Figure 3

based upon bleaching 7,000 pounds (28,000) yards of cloth of a definite construction, namely, 39"—80x80—4.00 percales, although this is not necessary because the formulæ in every case are based upon the weight of the goods regardless of their construction.

Peroxide Bleaching

The customary method of handling this cloth with peroxide is to give it a grey sour directly after singeing through 1½° Tw. sulfuric acid solution. Allow to stand for twenty to thirty minutes and wash thoroughly into the kier.

It is advisable to use a kier of the pump and heater type equipped with a circulation system to provide adequate flow of liquor through the goods. After loading the kier the cloth is given an alkaline pressure boil consisting of the following ingredients (percentage based upon the weight of the goods).

4% (280 pounds) solid caustic soda
1% (70 pounds) soda ash
.3857% (27 pounds) kier boiling assistant
.3428% (24 pounds) silicate of soda

After the boil, the cloth is washed down in the kier with warm water, and bleached in the same vessel. The bleaching is carried out by adding to a sufficient amount of water to operate the kier, ¾ to 1% hydrogen peroxide and 2% sodium silicate 82° Tw. The temperature of this bath is raised to 180° F. and the bleaching is carried out in four hours. At the end of this time the cloth is washed down in the kier with warm water and pulled out through a standard bleachery washer into the white bins.

The above outline gives the general method for handling this material under average mill conditions. It should be realized, however, that it may occasionally require some small changes to meet any unusual conditions and requirements.

Sodium Hypochlorite Bleaching

After boiling and washing the cloth as outlined above in the alkaline pressure boil, the cloth is pulled through a standard bleachery washer, squeezed, saturated with a 1° to 1¼° Tw. sodium hypochlorite solution, squeezed, pulled through four Gantt Pilers large enough to give the chlorine sufficient time to oxidize or bleach the discolored-oxidizable color of the cloth, pulled through another standard bleachery washer, squeezed, saturated with ¾° to 1° Tw. sulfuric acid, pulled through two more Gantt Pilers large enough to give the acid time to drive out the chlorine, and washed through the last standard bleachery washer into the white bins. In many cases sulfur dioxide (SO_2) has superseded the acids above, which will be discussed later.

Sodium Hypochlorite Solutions

Chlorine gas is unstable in water alone, it requires 3 pounds of soda ash or 1.3 pounds of caustic soda per pound of chlorine to keep it in a stable condition. In making sodium hypochlorite solutions suitable for bleaching textile fabrics, it is customary to make them at strengths of about 2.25%, no higher than 2.5%, as considerable difficulty is encountered in attempting to make the higher concentrations without special arrangements for keeping the solution cool. Above a temperature of 85° F. chlorates are formed which are non-effective.

The well known reaction for formation of sodium hypochlorite is: $2NaOH + Cl_2 = 2NaOCl + H_2O$. Above a temperature of 85° F. the non-effective chlorates are formed according to the following reactions: $3NaOCl = NaClO_3 + 2NaCl$.

In practice the alkali content of the sodium hypochlorite solutions are increased from 19.53% to 29.22% above the figures already given, and, as caustic soda adds more stability to the mixture than soda ash, they are used in conjunction with each other. In this way a good balance can be struck between the accelerating and the retarding action of the two stabilizers for liberating chlorine. The amount of excess alkali depends entirely upon the stability required, and how long it is desired to keep the solution. As temperature plays an important part in the stabilizing influences of sodium hypochlorite, formulæ vary in different climates and during different seasons of the year according to the following proportions:

	Summer North	*Summer South*	*Winter*
Water	500 Gals.	500 Gals.	500 Gals.
Soda ash	200 Lbs.	180 Lbs.	220 Lbs.
Caustic soda ..	80 Lbs.	90 Lbs.	60 Lbs.
Chlorine gas ..	100 Lbs.	100 Lbs.	100 Lbs.
	2.247% Sol.	2.250% Sol.	2.247% Sol.

Antichloring

The next stage in bleaching after chemicing is the removal of alkaline-sodium hypochlorite, and in some cases iron, lime, and magnesium. Sulfuric acid, muriatic acid, and oxalic acid are quite necessary for the removal of substances of this kind, but in a great many mills sulfur dioxide (SO_2) has superseded these acids and it is becoming a popular procedure to use either it alone or in conjunction with them. If desirable the acids can be used either before or directly after the chemic in order to accelerate the bleach or to remove mineral deposits.

Liquid sulfur dioxide is a harmless liquor supplied in steel cylinders under pressure, and is bubbled through a sight glass as a gas into plain water which forms sulfurous acid ($SO_2 + H_2O = H_2SO_3$). When cloth saturated with a caustic soda solution of sodium hypochlorite is brought in contact with it, sulfuric acid is formed ($H_2SO_3 + NaOCl = H_2SO_4 + NaCl$), which neutralizes the caustic soda and completely changes the active chlorine to common salt. ($H_2SO_4 + NaCl + 2NaOH = Na_2SO_4 + NaCl + 2H_2O$). Concentrated sulfuric acid is supplied in glass carboys and steel drums. It is dangerous and difficult to handle. If it contains commercial impurities, it attacks practically all metals. On iron, corrosion is slow for acid exceeding 65%; on lead, for acid

(Continued on page 558)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

SEPTEMBER 11, 1933

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Thirteenth Annual Convention

(By wire from Chicago)

APPROXIMATELY twn hundred enthusiastic members of the Association, representing the various Sections, were in attendance at the Thirteenth Annual Convention held this past Friday and Saturday in Chicago. There was no election of officers at this time, and the Annual Meeting for this purpose will be held in New York City in conjunction with the meeting of the New York Section on December 8th.

The program on Friday evening was presented as published except that William H. Cady presided in place of Carl E. Bick. The papers by J. D. Sandbridge and B. H. Harvey scheduled for this session were cancelled for lack of time. An excellent vandeville entertainment was presented. The Saturday morning session proceeded as scheduled with the exception of the absence of Howard D. Clayton, who was to have presented a paper on "Sanforizing." The Saturday afternoon session was presented according to published schedule.

At the banquet session Saturday night, Carl E. Bick, Chairman of the Mid-west Section, introduced Arthur T. Brainerd, Chairman of the Arrangements Committee, who called upon individual members of the Committee to rise and receive applause. Mr. Bick then introduced John W. Eich, who acted as toastmaster and who in turn introduced Prof. Louis A. Olney as the first speaker, replacing Dr. E. H. Killheffer, who was unable to be present. Prof. Olney spoke with regret of Dr. Killheffer's absence and eulogized his work for the Association. President Robert E. Rose then gave an historical sketch of the Association and its work. G. D. Pratt, representing the British Society of Dyers and Colourists, was then introduced and he spoke of the possibilities of closer cooperation between the two societies. Prof. W. H. Spencer, Dean of the School of Business, University of Chicago, was then introduced and spoke at length on the economic situation and predicted success for the NRA.

Copper steins with the Association insignia were presented at the banquet as souvenirs. The Arrangements Committee is to be congratulated upon the excellence of its preparations and arrangements. The members of this committee are as follows: Chairman, A. T. Brainerd; Entertainment, E. F. Smith; Reception, A. J. Feit; Publicity, E. A. Johnson; Technical Papers, D. H. Powers and G. M. Markle (for the Mid-west Section).

The Annual Convention and Meeting for 1934 will be held in New York City. Complete stenographic report of all addresses and papers will be published in forthcoming issues of the Reporter.

Proceedings of the American Association of Textile Chemists and Colorists

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—A. Newton Graves, Secretary, care Franklin Process Company, Providence, R. I.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

NOTE. Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the AMERICAN DYESTUFF REPORTER.

A-2

Education—B.T.C., Lowell Textile Institute, 1932; also course in shorthand and typing.

Experience—None to date, interested in quantitative analysis, experimental dyeing, color matching, dye testing and dye identification. Ability to learn quickly and will go anywhere. 23 years old, single.

A-B-1

Experience—over twenty years' experience in the laboratories of various chemical manufacturers, four months' experience as second hand in dye house, familiar with all types of dyes and fibers. Thirty-nine years old. Will supply references.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-B-E-1

Education—B.S. in chemistry at C.C.N.Y. Working now on M.A. at Columbia.

Experience—7 years as dye tester and color matcher for dye manufacturer; 6 months skein silk and rayon dyer; 4 years textile chemist and dyer for cotton finishing concern; 2 months boss bleacher and 4 years as teacher of organic chemistry and dyeing. Age 38, single.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

A-E-2

Education—B.T.C., Lowell Textile Institute, 1933.

Experience—Assistant instructor in chemistry, Lowell Textile Institute. Member of scholastic honorary fraternity.

B-1

Education—educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

B-7

Experience—4 years as assistant to manager in ribbon mill; 2 years as boss dyer on veils, chiffons and silk skeins; 5 years as boss dyer on ribbons and skeins (cotton and silk); 7 years as boss dyer on spun silk (pure dye and fast) resisted colors; last 12 years as hosiery dyer on silk and cotton, silk-cotton, rayon or wool. 50 years old, married. References.

B-8

Education—Chemistry and Dyeing Department, Philadelphia Textile School.

Experience—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

B-D-F-1

Experience—Has held positions as general superintendent of a print and dye works and a finishing company; held a position as boss dyer in a bleachery for 6½ years and as a colorist on 11 printing machines for 3½ years; has held a position as boss dyer for 6½ years with a finishing company and received general training for 3½ years; and has also been dyer in a mill dyehouse. Desires position as superintendent, colorist, dyer or salesman and solicitor.

D-1

Education—Graduate textile course, 1911, Georgia School of Tech.

Experience—Has had experience in all branches of the textile industry but chiefly in sales work. Was at one time in the dyestuff business and later in hosiery manufacturing. Prefers Middle Atlantic or southern states.

F-1

Education—Textile Institute, Alexander Hamilton Inst., Extension work at Brown Univ., working knowledge of German.

Experience—Has had executive departmental work with all types of textiles manufacturers. Acquainted with all types of textile machinery, dyestuff application, laboratory practice, cost methods, and checking methods and processes. References.

A-B-3

Experience—Wide experience in several of the best print works in New England as plant chemist and application chemist. Has had practical experience in the supervision of several departments and in the development of processes. References furnished.

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13th ANNUAL CONVENTION

A complete stenographic record of papers presented and discussions occurring at the Annual Convention in Chicago on September 8th and 9th will appear in forthcoming issues of the Reporter.

AMERICAN
DYESTUFF
REPORTER

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CONCERTED COOPERATION

"IT is not necessary to say, and certainly I do not need to emphasize the fact that there is no shortcut to success. So far as industrial codes are concerned the Administration will not tolerate any slackers or dodgers in this struggle for better times. The National Industrial Recovery Act has teeth in it, but fortunately it has not yet been necessary to resort to coercion or driving methods, though some pressure has been applied in certain cases. To establish a code of fair practice with the NRA should be the burning desire of every business man in this country if he has at heart his own interests and the good of his fellow Americans. There is so much of value to labor, to industry and to the consumer that if properly understood there can be no holding back.

"Cooperation on the part of every individual within this association and within the dry-cleaning industry working in partnership with the government under a NRA code will accomplish the desired result. Let me moralize in a practical way by saying that cooperation is not a sentiment; it is an economic necessity. And with this thought in mind, be courageous, have faith, go forward."

Such were the concluding remarks of C. C. Concannon, Chief of the Chemical Division of the Bureau of Foreign and Domestic Commerce, in an address before the National Association of Dyers and Cleaners in Washington on August 15th. Directed as they were, to the dyers and cleaners, the remarks are no less applicable to all other branches of industry. The "rugged individualism" of the past no doubt played an important part in the development of our country, but what we need now is "concerted cooperation" to save it. The former has had its chance, it is no more than fair that the latter should have the necessary support of every business to determine its worth.

There are two important features of the present system of control that should be given a fair trial before being condemned. The first is the attempt to relieve unemployment and the second is to provide some sort of economic foundation so that business will be permanently improved and the conditions which brought about our most recent depression will be remedied to prevent repetition. Whether this will all be brought about it is impossible to state, although there are favorable signs. In the meantime it is necessary for all business men to find out once and for all by giving the NRA their support.

SIX MONTHS LATER

AFTER six months of the new administration what in your opinion is the most important change which has been brought about in our country? Men have been put to work, more people probably have more money to spend, there has been a gradual improvement in general business conditions and other factors have developed to show improvement; but to our mind one of the most effective changes has been in the *spirit* of the individual. It is impossible to measure this with any ordinary means, yet it is undeniable and of immense proportions.

One of the important factors in bringing about this change has been the attitude of the President himself. He has been able to set an example which other people were willing and anxious to follow. Many of those who are following are not altogether in sympathy with his policies and doubt their success but the mere fact that they are willing to support him is proof enough of the new spirit which is in evidence.

The circumstances under which the President took office were favorable to make the display of leadership which he has made but it must be said that he made the most of his opportunities. It is possible to show that not all of the President's policies have justified the hopes that have been tied to them but at the same time it is impossible to determine the very great extent of the new hope that has arisen in the hearts of millions. For this we should be thankful and encouraged.

RESEARCH

IN an editorial of August 26th printed in the New York *Sun*, much space was given to the subject of research and it will be particularly gratifying to members of the A.A.T.C.C. to learn that an address of their president, Robert E. Rose, as published in a recent issue of the REPORTER, under the title of "The Value of Research," was chosen to emphasize the importance of research in our past and present workaday world. It further emphasizes the growing importance of Associations such as the A.A.T.C.C. in all of our lives.

Aids Re-Employment Drive

Action by the various departments of Hercules Powder Company to support President Roosevelt's drive to increase employment and expand national purchasing power has been announced by officials of the company.

Approximately 400 additional men will be given employment at Hercules plants throughout the country because of the shortening of working time. Wage adjustments to equalize the shorter hours have been announced at the various plants.

Neocarmin W

By the use of the above named product, marketed by the Kali Manufacturing Company, the difficulties of fiber identification are said to be much simplified. It is claimed that Neocarmin W will identify any textile fiber in a few minutes as it gives a specific color to each kind of fiber, irrespective of whether the threads are in the form of a single or mixed fabric.

To identify, a sample of the fabric or yarn to be tested is immersed in the solution for 3 to 5 minutes. After removing from the solution the sample is rinsed in running water, quickly passed through water containing a trace of ammonia, again well rinsed and dried. Immediately after the rinsing the characteristic colors of individual fibers are evident.

For further information regarding this product and also an illustrated circular showing the colors produced on the various fibers write to the Kali Manufacturing Company.

New National Dyes

National Milling Yellow 3G—This is a new addition to the line of neutral dyeing colors for wool, pure and tin weighted silk. It is said to be characterized by good fastness to fulling, carbonizing and acids, very good fastness to light, water, washing and perspiration, and by excellent fastness to sea water, stoving, rubbing and hot pressing.

National Erie Black NCW—This has been added to the National line for the specific purpose of supplying the trade with a direct dyeing black suitable for white acetate silk effects. Its fastness to washing is said to be improved by aftertreatment with formaldehyde and further it is said to be easily discharged with hydrosulfite.

National Milling Red R—This is an addition to the National line of neutral dyeing acid colors and is said to be characterized by excellent fastness to milling, washing, sea water, perspiration and rubbing, and by good fastness to light, cross dyeing and alkali.

Sample swatches of the above mentioned dyes may be obtained from the National Aniline & Chemical Company.

Geigy Releases

The Geigy Company, Incorporated has issued circulars on the following:

Diphenyl Fast Scarlet 4 G S W and Diphenyl Fast Scarlet 4 B S W—The circular on these two dyes illustrates their affinities for the following fibers: rayon leaving delustered Celanese white, cotton and silk dyed by the one and two bath methods, cotton yarn, cotton and wool dyed union and cotton and wool speck dyed.

Erio Fast Orange G L—This is a new homogeneous level dyeing acid dyestuff said to be of outstanding fastness to light and claimed to have exceptional level dyeing properties and good fastness to hot ironing.

Erio Anthracene Rubine B—This new product is bluer and brighter than the older Rubine R and similar to the latter it is said to possess similar fastness properties, belonging to the class of level dyeing acid colors and claimed to be fast to light and perspiration and of good fastness to washing, water and sea water.

Copies of the above mentioned circulars may be obtained on request from the Geigy Company.

Southern Alkali Corporation

After substantial expenditures on properties and construction during the last two years, work is being actively pushed to complete the alkali plant at Corpus Christi, Texas, the joint project of the Pittsburgh Plate Glass Company and the American Cyanamid Company.

This part of the chemical program, contemplated by the two companies for Corpus Christi, will represent an investment of several million dollars. These capital requirements are being financed by the Pittsburgh Plate Glass Company and the American Cyanamid Company out of their cash resources, and the transaction does not involve the issuance of securities to the public.

The Southern Alkali Corporation, which was organized in 1931, is building and will operate this plant. The stock of the Company is owned jointly by Pittsburgh Plate Glass and American Cyanamid. Hugh A. Galt, President of the Columbia Alkali Corporation, Barberton, Ohio, and a director of the Pittsburgh Plate Glass Company, is the president of the Southern Alkali Corporation.

In an announcement issued recently, Mr. Galt stated that the activity resulting from this development will help to support the program of the President and the Administration to create new jobs and thus put men back to work and decrease unemployment. This construction will give work to large numbers of engineers, contractors, skilled and unskilled labor—not only at the plant in Corpus Christi but also at the steel mills and at the other factories which will manufacture the material and equipment.

Rayon Dyeing and Finishing-14

By **B. L. HATHORNE**
Consulting Textile Chemist

CHAPTER VII—DYEING AND FINISHING OF RAYON-CONTAINING HOSIERY

(*Continued from page 535, August 28 issue*)

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Scouring Procedure—Rayon, Real Silk and Mercerized Cotton Ladies' Hose

(Soft Water Available)

(Hose oiled with nominal amount good grade rayon oil)

Per 100 *Pounds Goods*

(1) Enter previously bagged goods.
(2) Add 3 lbs. neutral soap (olive, palm or red oil soap).
(3) Add 2 lbs. solvent containing scouring oil (mixture of sulfonated castor or similar oil and a solvent).
(4) Add 4 lbs. "Degumming Oil" (a mixture of sulfonated castor oil and water gloss. There are many available on the market).
(5) Raise bath to boil (fifteen to twenty minutes required).
(6) Boil one hour, or until silk is degummed.
(7) Drop bath.
(8) Rinse.
(9) Extract.
(10) Shake out hose to remove tangles.
(11) Rebag hose and hold for dyeing operation.

Discussion of Dyeing

As has been pointed out in the discussion regarding scouring, a large proportion of all rayon-containing hosiery is scoured and dyed in a single bath. Many of the advantages and troubles encountered have been thoroughly discussed under scouring. Under the heading of dyeing, we will discuss only those problems directly connected with the application of the dyestuffs.

In general, rayon-containing hose, exclusive of hose containing cellulose acetate yarns, are entered into the dye bath at the boil. It is usual practice to have the dye bath contain:—

(1) A scouring agent such as soap or soluble oil.
(2) A solvent to aid in the removal of oil and to retard the formation of lime and magnesium soap aggregates.
(3) Dyestuffs necessary to produce the required shade.

The most economical and successful procedures all follow the same general scheme. The goods are run at the boil without salt in the above-described bath for a short period of time. After five to ten minutes an addition of salt is made, common salt or Glauber's, being used according to the dyestuffs chosen, and the particular procedure observed. The dyeing is continued at the boil for another short period, a second addition of salt is made, and the dyeing is continued for another five to fifteen minutes. At the end of this period, the goods are sampled, matched if necessary, removed from the machine, extracted and dried in the usual manner.

The most important difference between the dyeing of regenerated cellulose rayon hose and hose in which cellulose acetate yarns are present is:—

Care must be taken that the temperature of the scouring and dyeing baths in which cellulose acetate-containing hose are treated, does not exceed 180° F. unless special precautions are observed or a special finish is desired.

The specialized problems encountered by the hosiery dyers are such that their choice of dyestuffs is extremely limited. The peculiar shape and tight stitch of the heel and toe portions of hosiery present particularly difficult problems in penetration to the hosiery dyer.

Because of the heel and toe problem, it is essential that only the most level dyeing dyestuffs shall be used.

Most of the direct cotton dyestuffs have a greater affinity for mercerized cotton than for the regenerated cellulose rayons (cupra-ammonium excepted) when said dyes are applied in light percentages. As it is essential that good union effects be produced between the mercerized cotton and regenerated cellulose section of the hose, only dyestuffs having a very great affinity for regenerated cellulose rayons can be used.

In the entire group of direct cotton dyestuffs, there are only a few that pass the two above listed requirements successfully. These dyestuffs have been of necessity independently determined by many hosiery dyers and are used in practically all hosiery dyeing plants.

The correct application of the above described group of dyestuffs to rayon-containing hosiery cannot result in the production of the close union effects today required by

the trade. Luckily many of the neutral dyeing acid dyestuffs have an affinity for rayons when applied in very light shades. This affinity has been duly capitalized upon by hosiery dyers and enables them to produce practically perfect unions on combinations of mercerized cotton and regenerated cellulose rayon. As is the case with the direct cotton colors, there are only a few of the neutral dyeing acid dyestuffs that satisfactorily answer all the requirements of the hosiery dyeing trade. The few dyestuffs that have proven to be satisfactory are used by practically all hosiery dyers.

As in the case of hosiery scouring procedures it is impossible to give really representative hosiery dyeing procedures or procedures that will work satisfactorily under an unknown set of conditions. Below will be found dyeing procedures that were successfully used in prosperous mills during 1930.

Dyeing Procedure—Rayon and Mercerized Cotton Ladies' Hose
(Soft Water Available)
(Scoured Hose)
Per 100 *Pounds Goods*

(1) Add 1 lb. soap to bath.
(2) Add necessary dyestuffs.
(3) Raise bath to vigorous boil.
(4) Enter previously bagged goods.
(5) Boil vigorously for ten minutes.
(6) Add 6 lbs. Glauber's salt.
(7) Continue boiling for ten minutes.
(8) Add 6 lbs. Glauber's salt.
(9) Continue boiling for ten minutes.
(10) Add 6 lbs. Glauber's salt.
(11) Continue boiling for fifteen minutes.
(12) Sample.
(13) When shade is attained drop bath.
(14) Rinse.
(15) Run five minutes in finishing bath.
(16) Drop bath, extract and board.

Rayon and Mercerized Cotton Men's Hose
(Soft Water Available)
(Greige Goods)
Per 100 *Pounds Goods*

(1) Add ½ lb. tri-sodium-phosfate to bath.
(2) Add 2 lbs. soap.
(3) Add 3 lbs. solvent containing scouring oil (mixture of sulfonated castor oil and a solvent).
(4) Add necessary dyestuffs.
(5) Enter hose.
(6) Boil vigorously five minutes.
(7) Add 10 lbs. Glauber's salt.
(8) Continue boiling fifteen minutes.
(9) Add 10 lbs. Glauber's salt.
(10) Continue boiling fifteen minutes.
(11) Sample.
(12) Rinse.
(13) Drop bath, extract and board.

Rayon, Real Silk and Mercerized Cotton Hose
(Soft Water Available)
(Greige Goods)
Per 100 *Pounds*

(1) Add 3 lbs. neutral soap (olive, palm or red oil soap).
(2) Add 4 lbs. "Degumming Oil" (a mixture of sulfonated castor oil and water gloss).
(3) Add 2 lbs. solvent containing scouring oil (mixture of sulfonated castor oil and a solvent).
(4) Add necessary dyestuffs.
(5) Raise bath to "hand warm" temperature (100-115° F.)
(6) Enter greige goods.
(7) Raise temperature of bath to boil during one hour.
(8) Add 5 lbs. Glauber's salt.
(9) Boil gently fifteen minutes.
(10) Add 5 lbs. Glauber's salt.
(11) Continue gentle boiling for fifteen minutes.
(12) Add 10 lbs. Glauber's salt.
(13) Continue gentle boiling for fifteen minutes.
(14) Sample.
(15) When shade is matched drop bath.
(16) Rinse.
(17) Run five minutes in finishing bath.
(18) Drop bath, extract and board.

Rayon, Real Silk and Mercerized Cotton Hose
(Soft Water Available)
(Scoured Goods)
Per 100 *Pounds*

(1) Add 5 lbs. neutral soap to bath.
(2) Add necessary dyestuffs.
(3) Raise bath to boil.
(4) Enter scoured hose.
(5) Boil gently 5 minutes.
(6) Add 5 lbs. Glauber's salt.
(7) Continue gentle boiling ten minutes.
(8) Add 5 lbs. Glauber's salt.
(9) Continue gentle boiling ten minutes.
(10) Continue gentle boiling fifteen minutes.
(11) Sample.
(12) When shade is matched drop bath.
(13) Rinse.
(14) Run five minutes in finishing bath.
(15) Drop bath, extract, and board.

Acetate, Regenerated Cellulose and Mercerized Cotton Men's Half Hose
(Soft Water Available)
(Greige Goods)
Per 100 *Pounds*

(1) Add 5 lbs. soap to bath.
(2) Add necessary dyestuff dissolved in 1 to 5 lbs. soap (depending on dyestuffs used).
(3) Raise bath to "hand warm" temperature (100-115° F.)
(4) Enter greige goods.

(5) Raise temperature of bath to 160° F. during one-half hour.
(6) Add 5 lbs. Glauber's salt.
(7) Continue dyeing @ 160° F. five minutes.
(8) Add 5 lbs. Glauber's salt.
(9) Continue dyeing @ 160° F. five minutes.
(10) Add 10 lbs. Glauber's salt.
(11) Continue dyeing @ 160° F. fifteen minutes.
(12) Drop bath.
(13) Extract and board.

Acetate, Regenerated Cellulose and Mercerized Cotton Men's Half Hose

(Soft Water Available)
(Greige Goods)

The preceding procedure allows acetate dyestuffs to dye slowly upon the fiber while the temperature of the bath is slowly raised to 160° F. This procedure has the unfortunate disadvantage of allowing a large proportion of the direct cotton dyestuffs to become dyed upon the mercerized cotton before the regenerated cellulose rayon is dyed.

In order to produce more pleasing unions between the mercerized cotton and regenerated cellulose rayon portions of the hose, some dyers prefer to proceed as in the preceding procedure, with this exception—the starting temperature is 160° F. rather than 110, and the bath is raised to 180° F. instead of 160° F. The use of a high starting temperature makes it necessary to use particularly level dyeing cellulose acetate colors.

Discussion of Bleaching

As in the case of the circular knit underwear field, purchasers of bleached rayon and rayon-containing hosiery have demanded that bleached fabric be delivered so highly bleached that dyers have often seriously overbleached the fabric in order to satisfy the customer's demands for a "clear white." Overbleached white hose have given such poor service that the demand has diminished considerably.

Particularly because hose-containing real silk often have to be bleached, and must match all-rayon hose in shade, peroxide of hydrogen has proven to be the best bleaching agent for rayon and rayon-containing hose.

A special wooden tub should be utilized for the bleaching operation and should be used for nothing else. In the construction of the tub the following precautions should be observed:—

(1) No iron used in construction shall come into direct contact with the bleaching liquor (use wooden pegs on false bottom, etc.)
(2) Use lead pipes and fittings inside the tub.
(3) Provide a false bottom under which a perforated lead steam pipe should be installed for heating purposes.
(4) A perforated "false" top shall be provided to hold the goods under the liquor as described in the procedure.
(5) All pipes and fittings inside the tub shall be covered with wood to prevent fabric from coming into direct contact with pipes.
(6) A cloth strainer shall be attached to the water inlet pipe to prevent particles of iron rust from entering the bleaching bath.
(7) Provide a tight-fitting wooden cover for the tub to keep it clean when not in use.

Bleaching Procedure—Rayon and Rayon and Real Silk Hosiery

Per 100 *Pounds Goods*

(1) Make up liquor:—
9 lbs. 11 oz. 100 volume hydrogen peroxide.
8 lbs. silicate of soda.
¼ lb. sulfonated castor oil.
(2) Volume of bath shall be twenty-five times the weight of the goods.
(3) Well scoured and thoroughly rinsed hose are entered into the bath at room temperature.
(4) The bath is raised to 130° F. during one hour, during which time the goods are constantly worked or "poled" by an operator.
(5) Shut off steam and "sink" goods with perforated top.
(6) Allow hose to stand in cooling bath for two hours.
(7) Transfer hose to dye machine.
(8) Run ten minutes in bath containing:—
1/16 oz. Indanthrene Blue 2GSZ
1/16 oz. Indanthrene Blue RZ
(These colors are insoluble vat colors but are nevertheless sufficiently dispersed in a water emulsion to act as efficient and relatively fast blueing agents.)
(9) Extract and board.

Discussion of Finishing

At the present time very little attention is paid to the possibilities of adding materially to the "hand" and appearance of hosiery by means of softening and finishing materials. It is very probable that competition will eventually force more careful attention to the production of a pleasing hand on hosiery. Most hosiery dyers apply some stock finishing material to their hosiery in the rinse following the dyeing operation, regardless of whether or not the material used produces the most desirable feel and appearance in the particular hose processed.

These so-called finishing compounds usually consist of one of the many softening agents offered the trade. Too often an emulsion consisting of an oil emulsified with a sulfonated oil is used. Such softening compounds increase the luster of hosiery. In the dull luster vogue of 1931 oils should not be used in hosiery finishing bath. A second objection to oils as hosiery finishing agents is the "thin" sleazy feel imparted by oil to loosely knit fabric.

Most hosiery is given a decidedly improved hand by the application of solid, rather than liquid, fats and waxes. Sulfonated tallow, and emulsified wax finish have proven especially satisfactory in this respect.

A few highly specialized finishes have recently appeared

on the market. More can be expected in the near future. The most noteworthy of these specialized finishes is the so-called "shower proof" hose.

The so-called "shower proof" hose that appeared on the market in 1929 were processed following the dyeing operation through two consecutive baths. The first bath consisted of wax emulsified with soap. The second bath was aluminum acetate.

It was thought that shower proof hose would appeal to the trade, because mud spots could be easily and completely dusted off as soon as the same became dry. To date the process attracted very little general attention.

Discussion of Boarding

Although the boarding operation is not a function of the dyer or the dye house, it is nevertheless so closely connected with the dye problem, that it is deserving of discussion here. Troubles encountered in the boarding room are often laid at the door of the dye house regardless of the actual facts in the case.

The great bulk of hosiery is extracted as completely as possible in order to speed up the subsequent boarding operation. Very sheer chiffon hose, whether made from real silk, rayon, or combinations of real silk and rayon should not be extracted as completely as other types of hose. Complete extraction of sheer hose often causes them to become completely dried in some places while they are being pulled over the drying forms. Such premature drying causes the hose to have an uneven and undesirable appearance after it is removed from the drying form. Proper control of the degree of extraction of water completely eliminates premature drying, thus improving the appearance of the finished hose.

Whenever possible, the so-called steam boards are used because the high temperature combined with the high rate of heat exchange between the board and the encased steam enables steam boards to dry hosiery rapidly and efficiently. The temperature of steam boards sometimes rises as high as 240° F., although good practice dictates a maximum temperature of 220° F.

Very sheer hose, particularly sheer rayon hose must be boarded on hot water forms in order to eliminate trouble from premature drying. In some instances, the temperature of these boards must be maintained as low as 140° F.

The highest temperature to which steam boards can be raised in practice is not sufficiently high to affect cellulose acetate yarns in any way.

It sometimes happens that an unusually high percentage of rayon hose come from the boarding room with minute breaks at the heel gore. Trouble of this sort is usually blamed on one of two factors:—

(1) Improper treatment within the dye house.

(2) The rayon manufacturer.

It usually happens that complaints due to trouble encountered at the heel gore during the boarding operation are not directly traceable to either of the two mentioned causes. The trouble can usually be traced to:—

(1) Hosiery design.

(2) Rough handling in the boarding room. (For example, boarders used to handling 150 denier rayon hose will practically ruin the first few batches of 100 denier rayon hose they handle.)

In these days of the dull luster hosiery vogue, it is important to note that hose produced on hot water boards at a low temperature finish a trifle less lustrous than hose dried on the steam boards.

(*To be continued*)

Testing of Natural Resins

A. W. C. Harrison—Farben-Chemiker 255,3 (1932)—The resins are of much greater importance in the paint and lacquer industry than in textile operations, but some of them are occasionally employed in textile work for special purposes, though under the general false name of "gums." Like the true gums, they vary widely in quality according to locality of production, care taken in collection and cleaning, etc., and not only in the degree of purity (freedom from dirt, chips, grass, and so on) but in the quality of the pure resin itself. Beside their outward aspect, nature of fracture, etc., the resins do possess certain specific and mensurable characters, such as specific gravity, softening point, melting point, acid number, and so on, which, although only averages of good grades of the product, are accurate and fixed enough to afford some reasonable means of judging from them the goodness of the lot in question. As usual, different methods have been recommended by different workers for the determination of some of these "constants," and so the figures, accurately determined, we may suppose, are given sometimes in a quite divergent manner in the different reference-works. To some extent, however, very divergent figures must be obtained by a single worker using his own standard method, when the raw material consists of a complex mixture—particularly in the case of fossil resins gathered in a locality where the different portions of the gatherings may include material, some hundreds of years old, and some only two or three years old, all in the same lot and all looking alike. Western African copal is usually of this mixed sort, while the kinds from East Africa and New Zealand are mostly thoroughly fossilized and so have reached a stationary quality.

Some valuable discriminatory information is given on the subject of characteristics of fracture.

As to the question of color, likewise carefully taken up, it may be pointed out that there is a difference between a product uniformly off-color because of the condition of the substance itself, and an accidental color due to the presence of colored impurities which may either not affect the use of the gum, or else can be removed easily.

Comparative melting-tests are carried out by fusing the samples, in coarse powder, in test-tubes of uniform diameter, closed with loosely fitting glass stoppers, in an oilbath, at about 260° C., for about three minutes, withdrawing and wiping the tubes, and breaking off the glass carefully. The cylinders of resin thus obtained, of equal diameter, can then be compared and valued

Washington News Letter

New Means of Design Security

By WALDON FAWCETT

NOT counting the administrative steps recently taken at the U. S. Patent Office to simplify and accelerate the routine of patenting textile designs, two fresh developments will, this autumn, characterize the evolution of design insurance. Both are an answer to that spirit of desperation, which recently led certain extremists to go so far as to propose to trade associates that racketeers be employed to go into the plants of notorious copyists in the silk industry and smash the machinery.

In its legal aspects, the whole subject of the protection of original designs and color plans for textiles will be reopened the latter part of August when an effort will be made to secure the endorsement of the American Bar Association for an amended Design Registration or Design Copyright Bill to be laid before Congress at its next session. Balancing this in promise, is an inter-industrial ambition which will seek to adapt to the cause of mutual recognition of property rights in textile designs, the machinery of group control fostered by the National Industrial Recovery Act.

Decision within the textile industry to again appeal to Congress to provide a medium better suited to textile design protection than the present patent system, does not mean that there is lack of appreciation in trade circles of the current effort to cut red tape at the Patent Office. Rather is the new move expression of a conviction that the existing system of design patent, however efficiently administered, is incapable of affording the shelter against imitations or infringements needed by textile patterns which are original creations but are not "inventions," according to a strict technical construction of the term.

For members of the textile industry, who have designs eligible for admission as patented designs, the new short cuts in examination and enrollment at the Patent Office are unquestionably an advantage. Obviously so, in the case of seasonal designs. And, lest some readers of the REPORTER are not conversant with the preferential treatment now accorded to textile designs, it may be well to present the new status, as described for the REPORTER by James A. Brearley, Chief Clerk of the Patent Office.

Textile design cases have been made "special." That is to say they are acted on as soon as possible after being filed. The Patent Office has informed attorneys for textile firms that where they file an application for a textile design and accompany the same by a photographic print in addition to the regular drawing (such a print as is placed in each application by the Patent Office) the design application will go immediately to the Design Division.

This shortens the time that the applicant has to wait for action on his case. As a usual thing, those which are allowable can be passed to issue in about a week or a little over. The patent number is sent out by the Issue Division with the notice of allowance, so that the applicant, upon receiving his notice of allowance, has the information as to the date of issue and the number of his patent.

The Patent Office is also cooperating with the textile industry, latterly, by allowing its members to file photographs or photo-lithographs, in lieu of pen and ink drawings in India ink. This has resulted in a reduction of the cost of making drawings and has also resulted in the Patent Office obtaining a "drawing" which is of much better execution than the ordinary pen and ink drawing. For the sake of vividness and fidelity of reproduction of textile designs it appears that in some instances better results are obtained by the photographic method, whereas, in other cases, the results are superior by the photo-lithographic method. The Patent Office suggests that, on this score, textile men consider each design to be patented as a separate problem.

Leading advocates of enforced respect for originality in textile design will make it clear to Congress in January that their quarrel is not with the efficacy of the reforms at the Patent Office but with the chronic limitations upon the admissability of designs. As expressed for the REPORTER by Horace B. Cheney: "The reforms initiated at the U. S. Patent Office have been a decided help in making the patenting of designs a possibility. They do not by any means alter the necessity for legislation allowing the copyrighting of designs. Patenting is intended to protect invention and afford a monopoly of its use. There is very little actual invention in design. Copyrighting is a prohibition against copying others' work."

Chairman Henry D. Williams of the Committee which will present a Design Copyright Bill for the endorsement

of the American Bar Association, speaking of the rearrangements at the Patent Office, said:— "It may lessen the need; it cannot avoid the necessity for design registration. Textile designs are not proper subject matter for patents and cannot receive the protection to which they are entitled unless that protection is by copyright." Mr. Williams believes that with the copyright program limited to textiles it will be possible to secure action by the present Congress.

A school of thought in the textile field, supported by legal advice, holds that it should be possible to repress design piracy by condemnation in the codes of fair competition adopted under the National Industrial Recovery program. Mr. Sylvan Gotshal is one of those who feels that action under the National Recovery Act may help in the design dilemma. Defenders of design integrity in the textile field, who look hopefully to the Industrial Recovery Act, base their faith on two conditions which have never previously been present. One consists in the possibilities for the application of pressure to be found in the licensing system. The other arises from the participation by industry in terms of approximately 100 per cent of its strength. Virtually unanimous concurrence upon ethics of design observance would, of course, outdistance the best percentage of cooperation which has been obtainable in voluntary regimentation such as may be found in the Trade Practice Conferences sponsored by the Federal Trade Commission and in the varietal rationing carried out under the auspices of the Simplified Practice Division of the National Bureau of Standards. To qualify for correction under the Industrial Recovery program it should, seemingly, be necessary only to demonstrate that raids upon exclusive designs are as uneconomic for the industry at large as is price-cutting, or the recourse to "loss leaders."

KIER BOILING, BLEACHING AND ANTICHLORING

(Continued from page 546)

less than 65% whereas the gaseous-acid water SO_2 does not strongly affect either lead or iron. At low concentrations muriatic acid and sulfuric acid solutions should, therefore, be stored in lead-lined tanks fitted with lead pipes.

When cloth saturated with alkaline sodium hypochlorite is passed through a sulfuric acid solution, all free alkali is neutralized, the sodium hypochlorite is broken up, bleaching is accelerated, and chlorine driven off into the air. With sulfurous acid all free alkali is also neutralized, but the active chlorine instead of being driven off into the air, is converted into ordinary table salt by the strong reducing action of the sulfurous acid upon the sodium hypochlorite.

Sulfuric acid is used as an antichlor in very much higher concentrations than the acid derived from sulfur dioxide, and water. The usual running strength of sulfuric acid is about 1% or 1° Tw.; of sulfur dioxide 0.025% ($40/H_2SO_4 : 1/SO_2$). In the one case the cloth leaves the sour box saturated with 1° Tw. sulfuric acid and in the second case it is left in a practically neutral state. Sulfuric acid is difficult to remove and requires much more machinery and water to remove it than is required for rinsing out the harmless salts formed in the low concentration sulfurous acid method. Besides this, there is less labor involved, less wear and tear on the goods, and no danger of tendering the cloth as there is in drying the least trace of sulfuric acid in the cloth. It is not possible for sulfurous acid to be dried in the cloth on account of the water passing off as steam which liberates sulfur dioxide gas in the form of a vapor

$$(H_2SO_3 = H_2O + SO_2).$$
Steam Vapor

The strength of the sulfuric acid solution in the sour box is determined by titration. It is regulated by feeding a ten degree Tw. solution into water and maintaining a strength of one per cent. The strength of the sulfur dioxide is also determined by titration, it is regulated by bubbling it into water until a slight odor of the gas is noticeable and then closing the valve on the cylinder container to a point where the solution will maintain a strength of 0.025%.

My personal experience in depending upon the operator's sense of smell to warm him that the flow of SO_2 gas was exceeding the speed limit has been that he failed to heed the warning which this odor should have produced, or that he preferred the excess gas to going to the trouble of titrating the solution; nevertheless, it is an excellent indicator and, if used, it contributes a means of controlling the strength, which sulfuric acid does not possess.

A more detailed account of the uses of sulfur dioxide in the textile industry appeared in the March 13, 1933, and July 20, 1931, issues of the AMERICAN DYESTUFF REPORTER, written by A. K. Scribner, Virginia Smelting Co., West Norfolk, Va.

New Quaker Representative

The Quaker City Chemical Company announces the addition to its staff of Southern representatives of Mr. Woods Wilson Huff, son of Mr. J. H. Huff, Manager of the Rockwood Mills.

Mr. Huff, Jr., will be attached to the Knoxville, Tennessee plant of this Company.

THE DEVELOPMENT OF THE STABILIZED INSOLUBLE AZO DYES IN FAST COLOR PRODUCTION

By P. L. Mann

PROBABLY the most important feature of recent dyeing research is that relating to the fastness of dyed fabrics, and few fields of research are likely to have so profound an influence on the technique of dyeing and on the production of new dyestuffs. The demand for fast colors is increasing and has undoubtedly stimulated research activities in this field both in Germany and Great Britain as well as in this country. Therefore a survey of the development of Rapid Fast, Rapidogen, and Rapidozal colors, their constitution and application, will prove of interest.

The production of insoluble azo colors on the fiber is one stage, i.e., without the necessity of applying the active and passive components separately, has been the subject of many investigations. In the case of Nitrosamine Red, the nitrosamine, $C_6H_4(NO_2).N{=}N.ONa$, is obtained by adding diazotized para-nitraniline to excess of caustic soda, and as such is incapable of coupling with beta-naphthol. The printing color is made by mixing caustic soda, beta-naphthol, nitrosamine red, acetate of soda and a suitable thickening, such as gum tragacanth, and it is printed on white unprepared cloth. The goods are gently dried after printing, and subjected to air exposure for two or three hours, before being passed through a bath of dilute acid, after which they are washed and dried. The combined action of the carbonic acid of the air and the dilute acid bath liberates free diazotized para nitraniline from the nitrosamine red, which instantly couples with the beta-naphthol.

Nitrosamine or paramitro-ortho-anisidine may also be used. This, however, is not generally satisfactory, owing to the alkali liberated on formation of the red. This difficulty was overcome by E. A. Fourneaux who made an addition of suitable acid ethers to the printing color. These ethers were hydrolyzed by the liberated alkali so as to neutralize the injurious effect of excessive alkali. Ethyl oxalate, methyl formate, acetin, chlorethyl alcohol and dechlorhydrin are suitable ethers.

The next improvement consisted in printing a thickening mixture of Nitrosamine Red and the basic magnesium salt of 2-naphthol-1-sulfonic acid, drying, steaming, or permitting to lie until developed. During the steaming or lying the sulfonic group is split off and the diazo-compound couples it into position, thus yielding the same para-red. Later, the 2-naphthol-1-sulfonic acid was replaced by 2-naphthol-1-carboxyl acid, which couples with diazo-compounds, the carboxyl group being split off. This latter process has the advantage because it does not form difficultly soluble and stable salts with the liberated diazo-compounds which is the case with naphthol sulfonic acid.

The next important advance was made with the introduction of Rapid Fast colors. These consist of concentrated mixtures of the alkali metal salts of nitrosamines and an arylamide of 2:3-hydroxy-naphthoic-acid. Recently the range has been extended to include mixtures of nitrosamine-alkali salts and alkali salts of other passive components such as bodies containing a methylene group capable of coupling with diazonium compounds and arylamides of 2:3-hydroxy-carbazole-carboxylic acid. The arylides may be used in the form of their dry alkali metal salts or as free hydroxy-compounds. A normal salt capable of binding water is also added, the danger of explosion ordinarily inherent in nitrosamines is thereby minimized. When the early products were marketed they were in paste form, today they are manufactured as powders. For example, Rapid Fast Blue B is a mixture consisting of the potassium salt of the nitrosamine of tetrazotized dianisidine, the anilide of 2:3-hydroxy-naphthoic acid, and sodium acetate. Rapid Fast Red GZ consists of a mixture of a sodium salt of the nitrosamine of diazotized 2:5 di-chloraniline and the anilide of 2:3-hydroxy-naphthoic acid, sodium acetate being contained to bind the water. Rapid Fast Yellow G consists of the nitrosamine of diazotized 2:5 dichloraniline and diacetoacetic-ortho tolidide.

The print colors are made by pasting the Rapid Fast color with cold water and potassium or sodium chromate, adding a thickening such as tragacanth, and a little oleine oil and turpentine. After they are dried they are aged and developed in a hot solution of sodium sulfate in ½° Tw. acetic acid.

The Rapidogen dyestuffs belong to one of the two following mixtures: The first consists of a condensation product of a diazo-, tetrazo-, or diazotized amino-azo-compound with a secondary base containing no sulfonic or carboxylic acid or etheral sulfite group, e.g., piperidine, dimethylamine, etc., together with a suitable coupling component.

The mixture undergoes no decomposition in water or organic solvents even at 100° C. It is pasted with caustic soda, Turkey Red oil, and thickening medium and printed on unprepared cloth. Ageing is unnecessary and the colors are developed at 80° C. in a bath of 5 per cent formic acid and 10 per cent sodium sulfate. The formic acid splits up the amino-azo compound regenerating the diazonium compound which couples with the passive component. The sodium sulfate prevents the naphthol from dissolving off of the fiber previous to coupling. A suitable printing paste is composed of 11 parts (in weight) 5 - nitro-2-methoxy - 1 - benzene - azo - dimethylamine, 15 parts 2:3 hydroxy-naphthoyl-para-anisidine, 10 parts caustic soda (40 per cent), 30 parts Turkey Red oil, 600 parts starch-tragacanth, and 337 parts water. A red shade is obtained after printing, drying and developing, the insoluble azo color formed on the fiber being the same as that produced when diazotized Fast Red Base B is printed in Naphthol AS/RL. The condensation products

of diazo-compound with secondary bases may be represented by the following equations:—

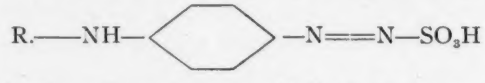
$$R.N:N.Cl + HN(CH_3)_2 \rightleftharpoons HCl + R.N:N.N(CH_3)_2$$

$$R.N:N.Cl + HNC_5H_{10} \rightleftharpoons HCl + R.N:N.NC_5H_{10}$$

The other alternative composition of Rapidogen dyestuff is one in which a water soluble diazoamino compound is incorporated in the dry state with a coupling component. The diazoamino compound is prepared by reacting a diazo compound with a primary or secondary amine of the benzene series, containing a carboxylic or sulfonic acid group of both. The compounds are stable towards heat, percussion, friction, neutral and alkali substances. As an example, Diazotized 3-chor-aniline is run at 0-10° C. into a neutral solution of 2-amino-4-sulfobenzoic acid in presence of sodium acetate. After stirring for an hour, the free diazo-amino acid separates as a yellow substance. Other appropriate stabilizing agents are 4- and 5-sulfo-2-amino-benzoic acids, methylamino-acetic acid, amino-benzene-2-:5-disulfonic acid, carcosin, butylamino-acetic acid, cyclohexylamino acetic acid, dibenzylamino-disulfonic acid, etc.

The introduction of Rapidogen dyestuffs presents no new problems in direct printing. The regular manner is adopted in preparing the goods, and the existing equipment for printing is employed. The ordinary precautions made at all times in the dyeing of rayon goods is, of course, essential. The advantage of Rapidogen colors over Rapid Fast colors is the greater stability of the printing pastes and the improved fastness to rubbing.

The first member of a new series of dyestuffs is the introduction of Rapidozol Blue, which consists of a passive component (or its alkali salt) and the alkali salt of a diazo-sulfonic acid or a diazo-hydrazine sulfonic acid. The diazo-sulfonic acids used are of the general formula



wherein R may represent a radical of the benzene or naphthaline series or an acyl radical. The aryl amino group may be substituted in the benzene range by halogen, alkyl or alkoxyl groups. As an example, 39.8 parts 4:4[1] diamino-diphenylamine are tetrazotized by means of 115 parts hydrochloric acid (33 per cent) and 28 parts sodium nitrate. The resulting solution is poured at 10-15° C. into a solution of 56 parts anhydrous sodium sulfite and 32 parts sodium carbonate in 750 parts water. On adding common salt to the brown solution the sodium salt of diphenylamine-4:4[1]-bis-diazosulfonic acid precipitates in the form of small brown crystals. The printing paste may consist of 63 parts of this product, 25 parts Naphthol AS, 30 parts caustic soda (40 per cent), 362 parts water and 500 parts starch-dragon. The fabric is steamed for seven or eight minutes after printing when sulfur dioxide is eliminated, and coupling occurs. A bluish-black of beautiful appearance is obtained after rinsing and soaping.

Appointed Works Manager

E. T. Woods, plant engineer of the National Oil Products Company, Harrison, New Jersey, has been appointed Works Manager of that company. He will have charge of the production and maintenance departments and the laboratories, and will retain his position of plant engineer.

Mr. Woods, who was born in Lexington, South Carolina, graduated from Clemson College, with the degree of B. S. in mechanical and electrical engineering. Prior to joining the National Oil Products Company, he was engineer for the Southern Cotton Oil Company, and also the American Linseed Company. He has been associated with his present organization since 1930. His home is in Arlington, New Jersey.

Columbia Textile Courses

Evening textile courses at Columbia this fall include the following: Spinning and Weaving of Cotton; Manufacture, Weaving and Converting of Rayon Yarns and Goods; and Design for Textiles. Fees for all courses are $20 plus $7 for registration. A consultation period with instructors has been arranged for every night except Saturady beginning September 20th from 7:30 to 9 P. M. Classes start Thursday, September 28th.

Acid Dyestuffs (Anthraquinone Series)

German Patent No. 465,435 (30/VIII/'28)—*I. G. Farben-Ind. A.-G.*—According to German Patent No. 462,799, o-amino-anthraquinone thiohydrines, when treated with acid condensing agents, give thiomorpholines of the anthraquinone series.

Such products, according to the present patent, are sulphonated, thus yielding dyestuffs valuable, e.g., for acetate silk.

Two examples, a strong reddish brown, and a green, each on wool from an acid bath, are given.

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Chemist required for Research and Development Work, with experience in weighting, dyeing and finishing. All communications kept confidential. Address Box No. 780, American Dyestuff Reporter, 440—4th Ave., New York, N. Y.